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(54) Timber preservation

(57) A composition is disclosed for preserving timber by protecting against wood-decaying fungi, the composition comprising a metal-organic compound which contains boron linked through an oxygen atom to a divalent metal element or metal radical, and a carboxylic acid radical together with a suitable carrier. Zinc-boron, manganese-boron, and iron-boron compounds with neodeconoic acid may be used, optionally together with o-phenyl phenol, nonyl phenol or chlorinated phenols, in a hydrocarbon solvent. The composition is applied to timber by conventional impregnation methods and is shown to be effective against *Coniophora puteana*.

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SPECIFICATION

Timber preservation

The present invention relates to timber preservation. More particularly the present invention relates to a method of preserving timber by protecting against wood-decaying fungi by impregnation of a fungicidal composition containing one or more metal compounds.

It is known that certain metal soaps are effective fungicides for the protection of cellulosic materials. Compounds such as copper naphthenate and zinc naphthenate have long been in use in compositions for preserving timber.

More recently, various synthetic fatty acids have become commercially available, for example,2-ethyl hexanoic acid, isononanoic acid, neodecanoic acid and mixed branched chain acids in various carbon atom ranges. Certain of these have been found to produce soaps of copper and zinc having fungicidal properties comparable to those of copper and zinc naphthenates.

It has now been found that the fungicidal properties of zinc, copper and other divalent metals can be improved by combining such metals in compounds containing not only synthetic fatty acids but also boron.

Accordingly, the present invention provides a method of preserving timber which comprises impregnating timber with a fungicidal composition comprising at least one metal-organic compound which contains boron, at least one divalent metal element or metal radical, the boron atom and the divalent atom or atoms being linked through oxygen atoms, and at least one carboxylic acid radical, together with a suitable carrier therefor.

The method according to the invention achieves protection of timber against wood-decaying fungi such as *Coniophora puteana*.

According to this invention, the fungicidal compositions may be introduced into the timber by any of the well known processes which ensure that the fungicide is uniformly distributed throughout the timber.

The fungicidal composition are preferably uniformily distributed throughout the timber by means of vacuum impregnation, and sawn timber is particularly advantageously preserved by the method according to the invention.

The metal-organic compounds used in the method according to the invention and processes for their preparation are disclosed and claimed in U.K. Patent No. 972,804.

The carboxylic acid radicals are preferably derived from carboxylic acids containing eight to ten carbon atoms. It has been found that the neodecanoic acid (Versatic (Trade mark) 10) radical is particularly suitable on account of its good solubility and ease of processing.

A particularly preferred compound for use in the method according to the invention is zinc boron Versatate.

Suitable carriers in which the metal-organic compounds are dissolved are organic solvents preferably hydrocarbons and more preferably white spirit.

Previously proposed fungicidal compositions have usually contained not less than about 2 to 3% by weight based on the total weight of composition of divalent metal to ensure adequate protection of timber in all environmental conditions over a long period of time. Employing the compositions of the present invention much less metal is required to give adequate protection. This is particularly important for timber which is exposed to heavy rainfall since metal soaps may slowly leach through wet timber.

It has further been found that the fungicidal effect of the compounds used in the method according to the invention can be further enhanced by incorporating one or more substituted phenols of known fungicidal activity, for example, *o*-phenyl phenol, nonyl phenol and chlorinated phenols.

Thus, according to another aspect the invention provides a fungicidal composition comprising at least one metal-organic compound which contains boron, at least one divalent metal element or metal radical, the boron atom and the divalent atom or atoms being linked through oxygen atoms, and at least one carboxylic acid radical, and one or more substituted phenols together with a suitable carrier therefor.

It has been found that the use of divalent metals in the form described herein results in good fungicidal activity as compared with conventional compounds such as copper and zinc naphthenate.

Apart from the good fungicidal activity, two other advantages arise from the use of divalent metals in the form described herein. These are that greatly reduced amounts of fatty acid are required to solubilize the metal, and also that much higher concentrations of metal in solution in solvents such as hydrocarbon solvents can be obtained than is possible with the normal di-soaps of the metals with naphthenic or with synthetic fatty acids.

The present invention will be further illustrated by reference to a series of tests comparing the fungicidal properties of compositions of the present invention with a known commercially available fungicide used for treating timber.

The compositions which comprised zinc boron Versatate or zinc naphthenate (comparison) dissolved in white spirit in different concentrations were subjected to a series of tests, described below, using blocks of Scots pine *(Pinus Sylvestris)* sapwood which were subjected to infestation by the wood destroying fungus *Coniophera puteana*.

Example 1

Wood blocks sized 14.5 x 10 x 7 mm, were oven dried for 18 hours, coded and weighed. They were then transferred to a glass vessel which was evacuated of air down to a pressure of less than 10 mm of mercury and were then held at this presure for 10 mins. The fungicidal treating solution was then admitted to the vessel to cover the blocks which were left covered for two hours to ensure full and uniform impregnation. The blocks were removed from the solution, allowed to drain and then reweighed to determine the uptake of the fungicidal treating compound. The blocks were then allowed to dry slowly for three weeks and were then sterilized by exposure to 1.2 epoxypropane vapour followed by ventilation in sterile air. The blocks were then transferred aseptically to actively growing soil feeder block cultures of *Coniophera puteana* and incubated for six weeks at 22°C. At the end of this period the extent of overgrowth on the test blocks were noted. The blocks were removed from the culture, oven dried and reweighed so that the loss in mass of each block due to fungal decay could be noted.

From the series of tests conducted it was possible to determine the toxic limits for the individual treatment compounds; such toxic limits being defined as the interval between the concentration or loading which just permits decay and the next higher concentration which inhibits all decay. We found the following results from tests as described above comparing zinc naphthenate with a zinc compound of boron and Versatic Acid i.e. zinc boron versatate as described in British Patent Specification No. 972804.

Compound	Toxic Limited % w/w Zn in treating solution	Toxic Limits Kg Zn/m^3 wood
Zinc naphthenate (comparative)	0.63 - 1.00	2.80 - 4.50
Zinc boron Versatate	0.25 - 0.40	1.05 - 1.80

It may be seen that the quantity of zinc required to prevent growth of *Coniophera puteana* is very significantly reduced when applied in the form of the zinc boron versatate rather than as zinc napthenate.

Further tests were carried out where the treated wood blocks were subjected to a water leaching process prior to infestation to simulate conditions where the fungicides may be required to protect timber which is exposed to adverse weather conditions.

Example 2

Wood blocks, sized 14.5 x 10 x 7 mm, were impregnated with fungicidal compositions as described in Example 1 and allowed to dry slowly for three weeks. The blocks were then leached in deionised water according to the following procedure.

The treated wood blocks were vacuum impregnated with water and allowed to soak for two hours. The water was then poured away and a further 30 ml was added. The water was changed after 24 hours and 48 hours and thereafter at a minimum interval of 24 hours and a maximum of 72 hours until the water had been changed on a total of 10 occasions. The blocks were then placed in a well ventilated oven at 45 to 50°C in order to dry to a moisture content of about 20% by weight. The blocks were then sterilised and exposed to cultures of *Coniophera puteana* as described in Example 1.

The leaching process did in most cases cause some reduction in fungicidal activity, but the retained activity of the fungicidal compositions of the present invention was never inferior and in certain cases superior to the corresponding comparative metal naphthenate compositions.

Example 3

Each compound as indicated in the following Table, was dissolved in a 50/50 w/w mixture of toluene and hexane to give solution concentrations by mass of 2.2, 1.0, 0.47, 0.22 and 0.10% metal. Blocks of Scots pine (*Pinus sylvestris*) sapwood, 14.5 x 10 x 7 mm were dried in an oven at 105°C for 18 hours, cooled and weighed. Sets of six of these blocks were placed in glass vessels, weighted down with glass weights and then evacuated to a pressure of less than 10 mm Hg and held for 10 minutes. The treatment solution was then slowly admitted to the vessel until the blocks were covered with liquid. Air was then admitted to the vessel and the blocks were left for 2 hours to permit full and uniform impregnation with solution. The blocks were reweighed to determine the uptake of solution and thus the loading of metal.

The blocks were allowed to dry slowly for three weeks, after which four of each set of six were sterilized with 1,2-epoxypropane vapour for 24 hours and then ventilated in sterile air for 72 hours. The blocks were then transferred aseptically to actively growing soil feeder block cultures of *Coniophora puteana* and incubated for six weeks at 22°C. After this period the culture vessels were examined and the extent of overgrowth on the test blocks noted. The blocks were removed from the culture, any adhering mycelium scraped off and the blocks weighed, oven dried and reweighed so that the loss in weight of each block due to fungal decay could be calculated.

The toxic limits derived from the tests are given in the following Table.

TABLE

Toxic limits obtained against *Coniophora puteana*

Compound	Toxic limit % w/w metal in treating solution	kg metal/m^3 wood
Manganese boroversatate	0.47 - 1.0	1.80 - 4.05
Iron boron Versatate, unoxidised	0.47 - 1.0	2.00 - 4.30
Iron boron Versatate, oxidised	0.47 - 1.0	1.80 - 3.65

Iron and manganese salts are not conventionally used as fungicides for the treatment of timber. However, these results surprisingly show that manganese and iron boroversatate are effective against *Coniophora puteana*.

Apart from the increased fungicidal activity, two other advantages arise from the use of divalent metals in the form described herein. These are that greatly reduced amounts of fatty acid are required to solubilize the metal, and also that much higher concentrations of metal in solution in solvents such as hydrocarbon solvents can be obtained than is possible with the normal disoaps of the metals with naphthenic or with synthetic fatty acids.

CLAIMS

1. A method of preserving timber which comprises impregnating timber with a fungicidal composition comprising at least on metal-organic compound which contains boron, at least one divalent metal element or metal radical, the boron atom and the divalent metal atom or atoms being linked through oxygen atoms, and at least one carboxylic acid radical, together with a suitable carrier therefor.
2. A method according to claim 1, wherein the carboxylic acid radical contains eight to ten carbon atoms.
3. A method according to claim 1, wherein the at least one metal organic compound is zinc boron Versatate.
4. A method according to any of claims 1 to 3, wherein the timber is impregnated by vacuum impregnation.
5. A fungicidal composition comprising at least one metal-organic compound which contains boron, at least one divalent metal element or metal radical, the boron atom and the divalent metal atom or atoms being linked through oxygen atoms, and at least one carboxylic acid radical and one or more substituted phenols with a suitable carrier therefor.
6. A fungicidal composition according to claim 5, wherein the carboxylic acid radical contains eight to ten carbon atoms.
7. A fungicidal composition according to claim 5, wherein the at least one metal organic compound is zinc boron Versatate.
8. A fungicidal composition according to any of claims 5 to 7, wherein the substituted phenol is a chlorinated phenol, *o*-phenyl phenol or nonyl phenol.

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